

Gradient scaling phenomenon of piezoelectricity in non-piezoelectric polyvinylidene fluoride films

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Abstract

It has been well known that flexoelectricity can be exploited to generate an analogous piezoelectric response in non-piezoelectric materials. For the direct flexoelectric effect, the induced electric polarization is linearly proportional to the applied strain gradient. Therefore, it is logical to expect that such a piezoelectric response would be enhanced in the materials with reduced dimensions. In this paper, we will report our experimental observation of such a gradient scaling phenomenon of piezoelectricity in non-piezoelectric polyvinylidene fluoride (PVDF) films.

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I. INTRODUCTION

The inhomogeneous electromechanical energy coupling between the applied strain gradient and the induced electric polarization in solid crystalline materials was proposed by Kogan in 1964 [1], which can be written as

$$\mu_{ijkl} = \frac{P_i}{\nabla_k S_{jl}}, \quad (1)$$

where P_i is the induced polarization, ∇_k is the symbol representing the gradient with respect to the direction k , μ_{ijkl} represents the flexoelectric coefficient, and S_{jl} is the applied strain. In Kogan's studies, he attributed this new phenomenon described by his model to “*piezoelectricity*”. It was later realized that his use of the term, “*piezoelectricity*”, might not be accurate. In 1981, Indenbom *et al.* suggested using the term of “*flexoelectricity*” to define the effect since the physical mechanisms behind piezoelectricity and flexoelectricity are different [2]. It should be pointed out that it was de Gennes who first clarified the physical mechanism of an analogous effect in liquid crystals and coined the term, “*flexoelectricity*” [3].

The physical picture of the flexoelectricity in solid crystalline dielectrics is clear; it is the applied inhomogeneous strain that breaks the inversion symmetry and induces the electric polarization even in centrosymmetric crystalline dielectrics [4]. Therefore, an analogous piezoelectric response in a non-piezoelectric crystalline dielectric can be generated via flexoelectricity; the relationship between the effective coefficient of this analogous piezoelectric response and the flexoelectric coefficient can be written as [5]

$$d_{eff} = \frac{\nabla_k S_{ij}}{c_{ijkl} \overline{S_{ij}}} \mu_{ijkl}, \quad (2)$$

where d_{eff} is the effective piezoelectric coefficient of the dielectric, c_{ijkl} represents the elastic stiffness tensor of the dielectric; $\overline{S_{ij}}$ is the average strain distributed in the dielectric. Thus it is clear, from Eq. (2), that we should find a dielectric with a larger flexoelectric coefficient and reduce its dimensions to render the dielectric capable of possessing strong analogous piezoelectric responses.

In previous theoretical and experimental studies, the flexoelectric coefficient, μ_{ijkl} , was estimated to have an order of magnitude of e/a (e and a represent the electron charge and the atomic dimension of the unit cell of crystalline dielectrics, respectively), which is

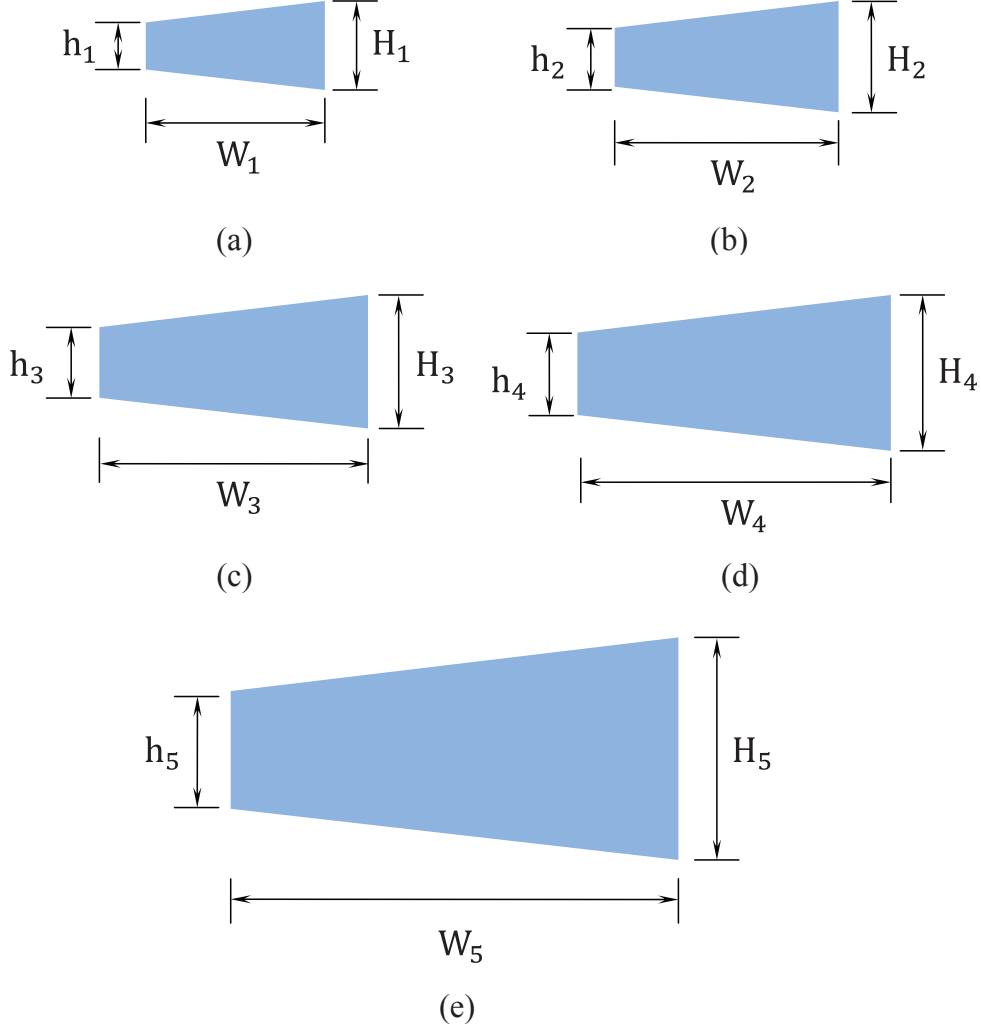


FIG. 1. The trapezoidal shaped PVDF films are shown here; these films are non-piezoelectric and their thickness is $22\mu\text{m}$. (a) $h_1 = 6\text{mm}$, $H_1 = 9.24\text{mm}$, $W_1 = 20.32\text{mm}$; (b) $h_2 = 7.5\text{mm}$, $H_2 = 11.55\text{mm}$, $W_2 = 25.4\text{mm}$; (c) $h_3 = 9\text{mm}$, $H_3 = 13.86\text{mm}$, $W_3 = 30.48\text{mm}$; (d) $h_4 = 10.5\text{mm}$, $H_4 = 16.17\text{mm}$, $W_4 = 35.56\text{mm}$; (e) $h_5 = 15\text{mm}$, $H_5 = 23.1\text{mm}$, $W_5 = 50.8\text{mm}$.

approximately equal to 10^{-10}C/m (see Ref.[1] and references therein). The next theoretical breakthrough was made by Tagantsev; in his seminal papers [6–8], he proposed that the flexoelectric coefficient should be proportional to the electric susceptibility in a crystalline dielectric, which can be written as

$$\mu_{ijkl} = \chi_{ij}\gamma_{kl}\left(\frac{e}{a}\right), \quad (3)$$

here χ_{ij} is the susceptibility of the dielectric under the mean field approximation, γ_{kl} is

an inhomogeneous susceptibility distribution tensor. This important relationship has been experimentally verified [9].

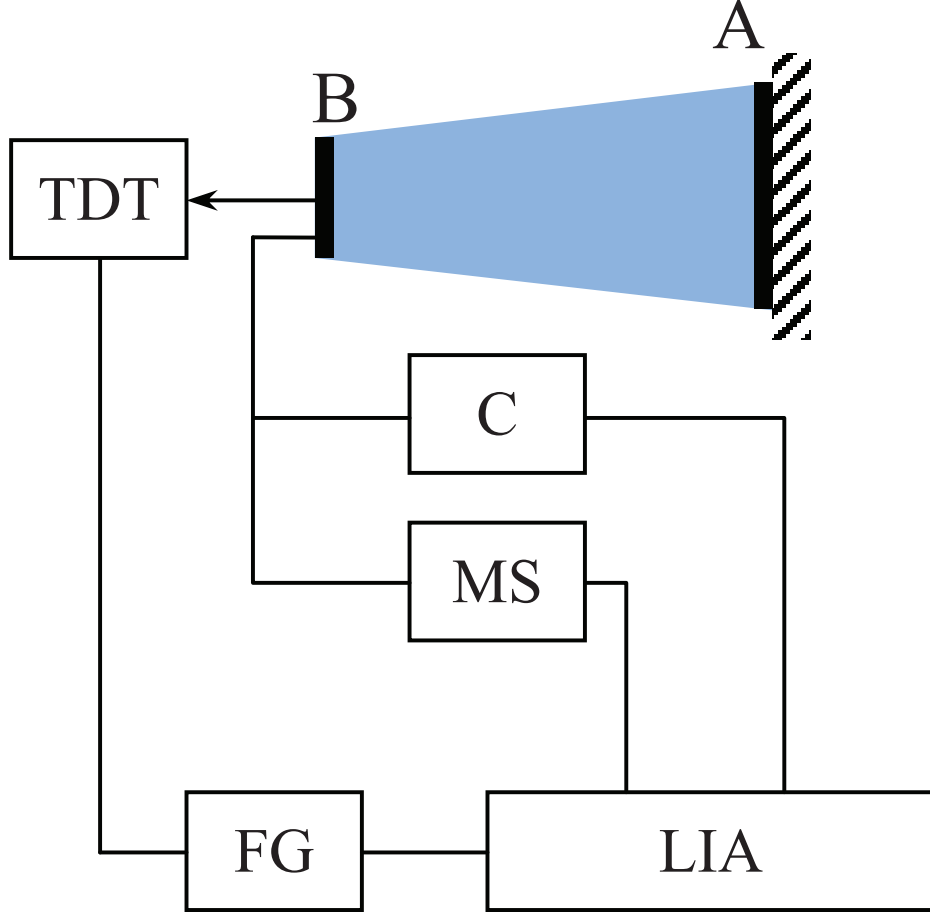


FIG. 2. Diagrammatic sketch of the lock-in detection setup for the measurement of the flexoelectric-type piezoelectric responses of the trapezoidal shaped PVDF films, which are defined in Fig. 1. The black stripes at A and B are electrodes; C: current measurement, FG: function generator, MS: MicroStrain DVRT probing sensor, TDT: tensile drawing tester, and LIA: lock-in amplifier.

In 1999, stimulated by Tagantsev's work, Fousek *et al.* proposed a method to fabricate some unique 0-3 piezoelectric composites, in which none of their components are piezoelectric [10]; for simplicity, we call this method as FCL method. The basic idea of the FCL method is to manipulate different non-piezoelectric components to form a composite with certain texture structures to generate the analogous piezoelectric response as required by the Curie group symmetry of the ensemble (composite). Since the charge separation mechanism

involved in the piezoelectric response of such a “*piezoelectric*” composite is flexoelectricity, we, for simplicity, call it as the flexoelectric-type piezoelectric composite.

Based on the FCL method, the first flexoelectric-type piezoelectric composite was developed by using a barium strontium titanate ($\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ or BST) composition in 2006 [5] and the gradient scaling phenomenon of piezoelectricity, i.e., as demonstrated in Eq. (2), the effective piezoelectric coefficient is inversely proportional to material dimensions, in the same composition was experimentally verified in 2007 [11]. The reason the BST composition was investigated in previous studies is that it has a large relative permittivity value, $\varepsilon_r \approx 16000$, at room temperature, which is just above its Curie temperature [12]. According to the Tagantsev’s model given in Eq. (3), it is not surprised that a giant flexoelectric phenomenon, $\mu_{12} \approx 100\mu\text{C}$, could be observed in this composition [12]. However, for most solid dielectrics, their flexoelectric coefficients are relatively small; besides, the solid dielectrics with large ε_r values are often stiff and fragile so that it is difficult to find a low-cost method to fabricate microscale structures by using these materials. Thus the solid dielectrics, which are suitable for the fabrication of low-cost flexoelectric-type piezoelectric composites with measurable piezoelectric responses, are rather limited.

The recent experiential observation of giant flexoelectric phenomena in polymers [13–15] may lead towards a low-cost and replicable method, which can be used to fabricate novel concept flexoelectric-type piezoelectric devices that are more flexible, lightweight, and low-cost. In previous studies of flexoelectricity of polymers, it was experimentally confirmed that the order of magnitude of the induced polarization to the deformation gradient ratio was approximately 10^{-11}C/m in elastomers [16]; theoretically, the relationship between the flexoelectric coefficient and electric susceptibility in polymers, which is similar to the Tagantsev’s model given by Eq. (3), has also been derived [17, 18]. However, experiential studies of flexoelectricity in bent-core liquid crystal elastomers (BCLCEs) [13] and in polyvinylidene fluoride (PVDF) films [14, 15] have shown that the previous conclusions on the flexoelectric behavior in polymers might not be accurate. It is perhaps interesting to point out that the PVDF film, in which a giant flexoelectric phenomenon, $\mu_{11} \approx 81.5 \pm 10\mu\text{C/m}$, was observed [15], has an average relative permittivity value of $\varepsilon_r \approx 11$ that is three orders of magnitude smaller than that of the BST. This indicates that the Tagantsev’s model might not be applied to the flexoelectric behavior of polymers; this is mainly because polymers possess the inherent rheological properties that distinguish the flexoelectric behavior in polymers from

that in solid crystalline dielectrics [19].

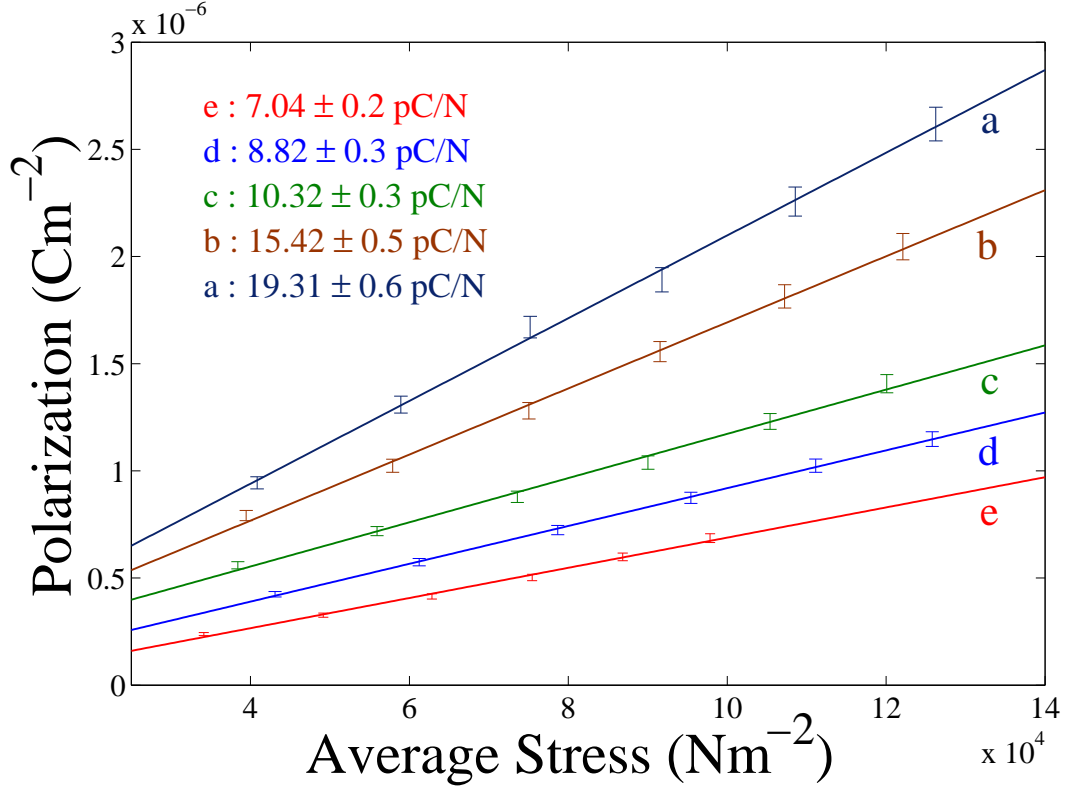


FIG. 3. Gradient scaling phenomenon of piezoelectricity in non-piezoelectric PVDF films; the effective piezoelectric coefficient, d_{eff}^i , of the trapezoidal shaped PVDF film labeled as i , which is defined in Fig. 1(i) ($i = a, b, c, d, e$), was measured at room temperature.

II. GRADIENT SCALING PHENOMENON OF PIEZOELECTRICITY IN POLYMER FILMS

The flexoelectric behavior in polymers is not only of great interest for its own sake, which would provide us with a broader perspective for understanding the dielectric properties of polymers, but it could also indicate a route to design novel soft flexoelectric-type piezoelectric devices. In these devices, the thermodynamic equivalence between the direct and the converse piezoelectric effects could be broken, but their properties do not violate equilibrium thermodynamics; i.e., such a device could only have the direct piezoelectric response but no converse piezoelectric response (a perfect piezoelectric sensor!) or vice versa (a perfect

piezoelectric actuator!) [20]. To fabricate such a device, ones have to find certain materials with strong flexoelectric responses and verify whether these materials possess measurable piezoelectric properties via flexoelectricity at micro- or nano-scale. In this study, we report the experimental observation of the gradient scaling phenomenon of piezoelectricity in non-piezoelectric PVDF films.

The preparation of the PVDF film being investigated and its XRD characterization have been given in Ref.[14] and will not be repeated here. The film is non-piezoelectric and was cut into the pieces with the trapezoidal shape shown in Fig. 1. The trapezoidal shape of a film sample will lead to the generation of strain gradient when the sample undergoes elastic tensile stretching. In addition, the film samples shown in Fig. 1 are unstretched and unpoled so that we could exclude possible extrinsic factors from our flexoelectric-type piezoelectric measurement. For the film samples with the trapezoidal shape, the relationship between the effective coefficients of their analogous piezoelectric responses and their flexoelectric coefficient can be further simplified as

$$d_{eff} = \frac{P}{E\bar{S}}, \quad (4)$$

where P and \bar{S} are the induced polarization and the average strain of the samples undergoing elastic tensile stretching, respectively; E is the Youngs modulus of the samples, which is around $E \approx 3.13 \times 10^9 \text{N/m}^2$ [14]. P can be estimated via the following relationship

$$P = \frac{I}{2\pi f A}, \quad (5)$$

where I is the induced electric current in the samples undergoing periodic tensile stretching, A is the area of the electrodes fabricated on the samples (the area of the black strip at the B end shown in Fig. 2), and f is the frequency of the periodic stretching. The corresponding flexoelectric-type piezoelectric measurement is summarized in the next section.

III. PIEZOELECTRICITY MEASUREMENT

The inhomogeneous strain values in the trapezoidal shaped PVDF films were generated by using a tensile drawing tester (TDT) shown in Fig. 2, which is modified from a commercial piezo actuator. The scheme of the lock-in detection setup, which is diagrammatically shown in Fig. 2, is summarized as follows: a function generator (FG) is used to provide an AC

TABLE I. The measured effective piezoelectric coefficients, d_{eff}^i ($i = a, b, c, d, e$), of the trapezoidal shaped PVDF films, which are defined in Fig. 1, are summarized here. The unit of d_{eff}^i ($i = a, b, c, d, e$) is pC/N.

Trapezoidal shaped PVDF films	d_{eff}^i
Sample a defined in Fig. 1(a)	$d_{eff}^a = 19.31 \pm 0.6$
Sample b defined in Fig. 1(b)	$d_{eff}^b = 15.42 \pm 0.5$
Sample c defined in Fig. 1(c)	$d_{eff}^c = 10.32 \pm 0.3$
Sample d defined in Fig. 1(d)	$d_{eff}^d = 8.82 \pm 0.3$
Sample e defined in Fig. 1(e)	$d_{eff}^e = 7.04 \pm 0.2$

sinusoidal signal with a frequency of $f = 0.5\text{Hz}$ to an amplifier to control the periodic elastic tensile stretching movement of the TDT and to a lock-in amplifier (LIA) as a reference signal; the deformation, ΔW_j ($j = 1, 2, 3, 4, 5$), at the B end are detected by using a MicroStrain DVRT probing sensor via LIA and the strain values at both A end, S_A^i , and B end, S_B^i , can be estimated as $S_A^i = (\Delta W_j \times h_j)/(W_j \times H_j)$ and $S_B^i = \Delta W_j/W_j$ ($i = a, b, c, d, e$; $j = 1, 2, 3, 4, 5$), respectively; here h_j , H_j , W_j , j ($j = 1, 2, 3, 4, 5$), and i ($i = a, b, c, d, e$) are defined in Fig. (1); the average strain values of the trapezoidal shaped films can be estimated as $\overline{S}_i = (S_A^i + S_B^i)/2$ ($i = a, b, c, d, e$). The induced electric current values, I_i ($i = a, b, c, d, e$), are measured via LIA, and the corresponding polarization values, P_i ($i = a, b, c, d, e$) are calculated by using Eq. (5).

Under the same physical conditions and at room temperature, we measured both P_i and \overline{S}_i ; the linear proportional relationship between P_i and the corresponding average stress value, which is defined as $E \times \overline{S}_i$, is shown in Fig. 3. For comparison the measured effective piezoelectric coefficients, d_{eff}^i ($i = a, b, c, d, e$), of the trapezoidal shaped PVDF films are

given in Table 1. From Fig. 3 and Table 1, we can see clearly, as expected from scaling, that d_{eff}^i ($i = a, b, c, d, e$) is inversely proportional to W_j ($j = 1, 2, 3, 4, 5$) in those trapezoidal shaped PVDF films. Therefore, the gradient scaling phenomenon of piezoelectricity does exist in non-piezoelectric PVDF films.

IV. CONCLUDING REMARKS

We have observed the gradient scaling phenomenon of piezoelectricity in non-piezoelectric PVDF films. The maximum effective piezoelectric coefficient we have obtained is about $d_{eff}^a = 19\text{pC/N}$; the corresponding dimension, W_1 , of the trapezoidal shaped PVDF film is 20.32mm. The results obtained in this study do suggest that a flexoelectric-type piezoelectric device fabricated by using non-piezoelectric PVDF films could generate huge effective piezoelectric responses if its size is reduced to the micrometer range. Our research indicates that flexoelectricity may provide a novel route to the fabrication of the low-cost flexible piezoelectric sensors and actuators with performance comparable to current commercialized ferroelectric polymer devices.

ACKNOWLEDGMENTS

We would like to thank Solvay Solexis for providing PVDF powders to us. The research reported in this paper was sponsored by the State University of New York at Buffalo.

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